There are rate equations similar to Eq. (13.45) for $O_2$, $N_2$, O, N, $NO^+$, and $e^-$. Clearly, you can see that a major aspect of such a nonequlibrium analysis is simply bookkeeping, making certain to keep track of all of the terms in the equations.

Values of the rate constants for high-temperature air are readily available in the literature. See, for example, [158–162]. Again, keep in mind that there is always some uncertainty in the published rate constants; they are difficult to measure experimentally and very difficult to calculate accurately. Hence, any nonequilibrium analysis is a slave to the existing rate data.

For temperatures above 9000 K, where ionization of the atoms takes place, a kinetic mechanism more complex than that given by Eqs. (13.40a–13.40g) is needed. Such a mechanism, along with the appropriate rate constants, is given in Table 13.2. These data were compiled by Dunn and Kang in [162], and the table is readily found in [158]. In this table, a form of the rate constant similar to that given in Eq. (13.33) is used, specifically

$$k_f = C_f T^{\eta_f} e^{-K_f/\mathscr{R}T} \tag{13.46}$$

where $\mathscr{R} = 1.986$ cal/(g · mol) K. The units of $k_f$ are expressed in $cm^3$, g · mol, and seconds, in the combination appropriate for the given chemical equation. A typical temperature variation for one of the reactions, namely, the $O_2 + O_2 \rightleftharpoons 2O + O_2$ reaction, is shown in Fig. 13.3. Clearly, the value of $k_f$ changes rapidly with temperature.

Table l3.2 and Fig. 13.3 are given here, not to say that the rate data are precise, because they are not. Uncertainties exist in all of these data. Rather, Table 13.2 and Fig. 13.3 are representative of the rate data in modern use and are given here simply to serve as an example. If you wish to carry out a serious nonequilibrium analysis, the suggestion is made to always canvas the existing literature for the most accurate rate data, even to the extent of talking with the physical chemistry community, before embarking on any extensive calculations.

### 13.4.1    Two-Temperature Kinetic Model

The temperature $T$ that appears in all preceding sections is labeled the translational temperature; it is a measure of the collective translational energy of the particles of the gas through Eq. (12.9a). It is the temperature that enters into the molecular collision frequency through Eqs. (12.18–12.20). Therefore, it is natural that the vibrational relaxation time $\tau$ is a function of $T$ through Eq. (13.19), and the chemical rate constants are functions of $T$ through Eqs. (13.32) and (13.33).

In the special case that both vibrational and chemical *nonequilibrium* simultaneously exist in a mixture of gases, there is a coupling between the chemical reaction rates and the vibrational relaxation rates that affects the values of each. Molecules that are highly excited vibrationally, that is, in the higher-lying vibrational energy levels, are more readily dissociated by molecular collisions. They simply require less energy exchange during collisions to dissociate. Therefore, the chemical kinetic rates for dissociation are going to be faster if

**Table 13.2    Kinetic mechanism for high-temperature air for the Dunn/Kang model**

| Reaction | | | | | $C_f$ | $\eta_f$ | $K_f$ |
|---|---|---|---|---|---|---|---|
| $O_2 + N$ | $=$ | $2O$ | $+ N$ | | 3.6000E18 | $-1.00000$ | 118,800 |
| $O_2 + NO$ | $=$ | $2O$ | $+ NO$ | | 3.6000E18 | $-1.00000$ | 118,800 |
| $N_2 + O$ | $=$ | $2N$ | $+ O$ | | 1.9000E17 | $-0.50000$ | 226,000 |
| $N_2 + NO$ | $=$ | $2N$ | $+ NO$ | | 1.9000E17 | $-0.50000$ | 226,000 |
| $N_2 + O_2$ | $=$ | $2N$ | $+ O_2$ | | 1.9000E17 | $-0.50000$ | 226,000 |
| $NO + O_2$ | $=$ | $N$ | $+ O$ | $+ O_2$ | 3.9000E20 | $-1.5$ | 151,000 |
| $NO + N_2$ | $=$ | $N$ | $+ O$ | $+ N_2$ | 3.9000E20 | $-1.5$ | 151,000 |
| $O + NO$ | $=$ | $N$ | $+ O_2$ | | 3.2000E9 | $1$ | 39,400 |
| $O + N_2$ | $=$ | $N$ | $+ NO$ | | 7.0000E13 | $0$ | 76,000 |
| $N + N_2$ | $=$ | $2N$ | $+ N$ | | 4.0850E22 | $-1.5$ | 226,000 |
| $O + N$ | $=$ | $NO^+$ | $+ e^-$ | | 1.4000E06 | $1.50000$ | 63,800 |
| $O + e^-$ | $=$ | $O^+$ | $+ 2e^-$ | | 3.6000E31 | $-2.91$ | 316,000 |
| $N + e^-$ | $=$ | $N^+$ | $+ 2e^-$ | | 1.1000E32 | $-3.14$ | 338,000 |
| $O + O$ | $=$ | $O_2^+$ | $+ e^-$ | | 1.6000E17 | $-0.98000$ | 161,600 |
| $O + O_2^+$ | $=$ | $O_2$ | $+ O^+$ | | 2.9200E18 | $-1.11000$ | 56,000 |
| $N_2 + N^+$ | $=$ | $N$ | $+ N_2^+$ | | 2.0200E11 | $0.81000$ | 26,000 |
| $N + N$ | $=$ | $N_2^+$ | $+ e^-$ | | 1.4000E13 | $0$ | 135,600 |
| $O + NO^+$ | $=$ | $NO$ | $+ O^+$ | | 3.6300E15 | $-0.6$ | 101,600 |
| $N_2 + O^+$ | $=$ | $O$ | $+ N_2^+$ | | 3.4000E19 | $-2.00000$ | 46,000 |
| $N + NO^+$ | $=$ | $NO$ | $+ N^+$ | | 1.0000E19 | $-0.93$ | 122,000 |
| $O_2 + NO^+$ | $=$ | $NO$ | $+ O_2^+$ | | 1.8000E15 | $0.17000$ | 66,000 |
| $O + NO^+$ | $=$ | $O_2$ | $+ N^+$ | | 1.3400E13 | $0.31$ | 154,540 |
| $O_2 + O$ | $=$ | $2O$ | $+ O$ | | 9.0000E19 | $-1$ | 119,000 |
| $O_2 + O_2$ | $=$ | $2O$ | $+ O_2$ | | 3.2400E19 | $-1$ | 119,000 |
| $O_2 + N_2$ | $=$ | $2O$ | $+ N_2$ | | 7.2000E18 | $-1$ | 119,000 |
| $N_2 + N_2$ | $=$ | $2N$ | $+ N_2$ | | 4.7000E17 | $-0.5$ | 226,000 |
| $NO + O$ | $=$ | $N$ | $+ 2O$ | | 7.8000E20 | $-1.5$ | 151,000 |
| $NO + N$ | $=$ | $O$ | $+ 2N$ | | 7.8000E20 | $-1.5$ | 151,000 |
| $NO + NO$ | $=$ | $N$ | $+ O$ | $+ NO$ | 7.8000E20 | $-1.5$ | 151,000 |
| $O_2 + N_2$ | $=$ | $NO$ | $+ NO^+$ | $+ e^-$ | 1.3800E20 | $-1.84$ | 282,000 |
| $NO + N_2$ | $=$ | $NO^-$ | $+ e^-$ | $+ N_2$ | 2.2000E15 | $-0.35$ | 216,000 |

the gas is already highly excited vibrationally. Similarly, because dissociation more readily occurs from the higher-lying vibrational levels, there is a preferential depopulation of the higher-lying vibrational energy levels when dissociation is going on, thus affecting the instantaneous vibrational energy of the gas and the vibrational relaxation time.

The precise accounting of this mutual coupling phenomena on both the vibrational and chemical rates is complex. An attempt to deal approximately with this coupling involves the definition of a vibrational temperature $T_{vib}$ as follows. Consider a given molecular species, say, $O_2$. If the instantaneous nonequilibrium value of vibrational energy per unit mass of this species is $e_{vib}$ as dictated by the vibrational rate equation (13.17), then we define an